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COPPER SALTS OF ORGANIC ACIDS AND USE THEREOF AS FUNGI-  
CIDES

The present invention relates to the use of copper  
10 salts of organic acids for the control of phytopathogen  
fungi.

Inorganic copper salts, such as, for example, sul-  
fates, oxychlorides, hydroxides, carbonates and the well-  
known Bordeaux mixture, have been widely used in agricul-  
15 ture for the control of fungal diseases in preventive ap-  
plications.

It is also known that copper salts of organic acids  
such as, for example, copper acetate, copper succinate,  
copper glutarate, copper adipate, copper citrate, copper  
20 tartrate, copper aspartate, copper glutamate, copper  
phthalates, copper benzoates, can be used for the control  
of fungal diseases in agricultural crops, optionally  
mixed with other active principles, as described, for ex-  
ample, in JP7398021; or in Pesticide (1980), vol. 14(10),  
25 pages 29-30; or in Geobios (1985), vol. 12(3-4), pages

147-8.

The Applicant has now found that copper salts of some particular organic acids allow a prolonged protective action to be obtained on vegetables, which is higher  
5 than that of the copper salts described above and with much lower doses.

The use of these salts in agronomic practice therefore allows, with respect to the previously known organic or inorganic copper derivatives, a reduction in the copper content in the formulates applied with significant  
10 beneficial repercussions on the environmental impact.

The Applicant has also found that these salts are an excellent form of controlling phytopathogens also in vegetable varieties genetically modified to amplify the  
15 original natural defense mechanism.

Furthermore, the Applicant has found that these salts can also be used for the control of fungal diseases on non-living substrates such as, for example, plastics, metals, textile fibres, glass, wood, paper, foams,  
20 bricks, etc. These salts can be applied on the surface of the substrate by methods well-known in the art, such as spraying, painting, immersion, impregnation, etc. at application doses depending on the nature of the material and conditions to which the substrate is subjected.

25 Many of these copper salts are new; others are

known, but their use has never been described for these particular applications.

An object of the present invention therefore relates to the use of compounds having general formula (I):



wherein:

- A represents the bibasic ion of an organic acid which can have the meanings (A<sub>1</sub>)-(A<sub>8</sub>);
  - 10 - Cu represents the copper 2+ ion;
  - (A<sub>1</sub>)-(A<sub>8</sub>) respectively represent the following carboxylic acids:
- (A<sub>1</sub>):

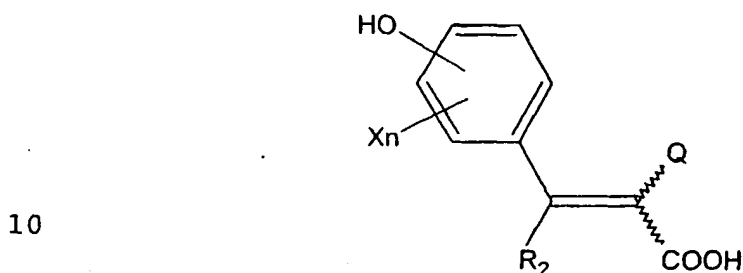


wherein:

- R<sub>1</sub> and R<sub>2</sub>, the same or different, represent a hydro-
- 20 gen atom; a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> haloalkyl group, linear or branched, optionally substituted; a C<sub>2</sub>-C<sub>6</sub> alkenyl or C<sub>2</sub>-C<sub>6</sub> haloalkenyl group, linear or branched, optionally substituted; a C<sub>3</sub>-C<sub>6</sub> cycloalkyl group, optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkoxy or C<sub>1</sub>-C<sub>6</sub> haloalkoxy group, linear
- 25 or branched, optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkylthio or

C<sub>1</sub>-C<sub>6</sub> haloalkylthio group, linear or branched, optionally substituted; a C<sub>3</sub>-C<sub>6</sub> cycloalkoxyl group, optionally substituted; an aryl group optionally substituted or a heteroaryl group optionally substituted; a heterocyclic  
5 group optionally substituted;

(A<sub>2</sub>):



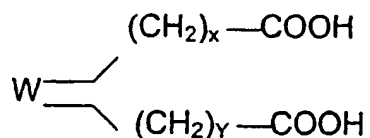
Wherein:

- R<sub>2</sub> has the meanings defined above;
- Q represents a hydrogen atom; a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub>  
15 haloalkyl group, linear or branched, optionally substituted; a cyano group; a C<sub>1</sub>-C<sub>6</sub> alkylcarbonyl or C<sub>1</sub>-C<sub>6</sub> haloalkylcarbonyl group, linear or branched, optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkoxycarbonyl group, linear or branched, optionally substituted; an aminocarbonyl group; a C<sub>1</sub>-C<sub>6</sub> alkylaminocarbonyl group;  
20 a C<sub>2</sub>-C<sub>12</sub> dialkylaminocarbonyl group;
- X represents a hydrogen atom or a halogen atom; a hydroxyl group; a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> haloalkyl group, linear or branched, optionally substituted; a  
25 C<sub>1</sub>-C<sub>6</sub> alkoxyl or C<sub>1</sub>-C<sub>6</sub> haloalkoxyl group, linear or

branched, optionally substituted; a cyano group; a  
 nitro group; an amine group; a C<sub>1</sub>-C<sub>6</sub> alkylamine  
 group; a C<sub>2</sub>-C<sub>12</sub> dialkylamine group; a C<sub>1</sub>-C<sub>6</sub> linear or  
 branched thioalkyl group, possibly substituted; a  
 5 C<sub>1</sub>-C<sub>6</sub> linear or branched halothioalkyl group, possi-  
 bly substituted; a C<sub>1</sub>-C<sub>6</sub> linear or branched alkyl-  
 sulfinyl group, possibly substituted; a C<sub>1</sub>-C<sub>6</sub> linear  
 or branched alkylsulfonyl group, possibly substi-  
 tuted;

10 - n is a number ranging from 1 to 4;

(A<sub>3</sub>):

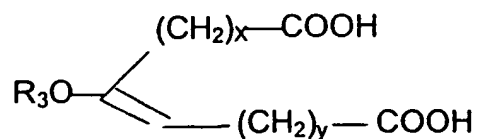


15 wherein:

- W represents an oxygen atom; a C<sub>1</sub>-C<sub>6</sub> alkylimine  
 group, linear or branched, optionally substituted; an  
 arylimine group optionally substituted; a heteroarylimine  
 group optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkoxyimine group,  
 20 linear or branched, optionally substituted; an aryloxy-  
 imine group optionally substituted;

- x and y, the same or different, are a number ranging  
 from 0 to 4;

(A<sub>4</sub>) :



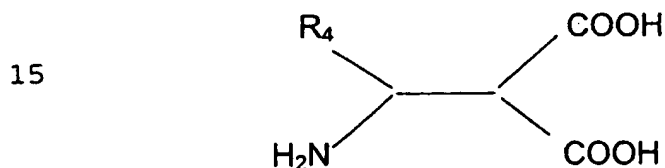
5 wherein:

- R<sub>3</sub> represents a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> haloalkyl group, linear or branched, optionally substituted; a C<sub>3</sub>-C<sub>6</sub> cycloalkyl group, optionally substituted; an aryl group, optionally substituted; a heteroaryl group, optionally

10 substituted;

- x and y, the same or different, are a number ranging from 0 to 4;

(A<sub>5</sub>) :

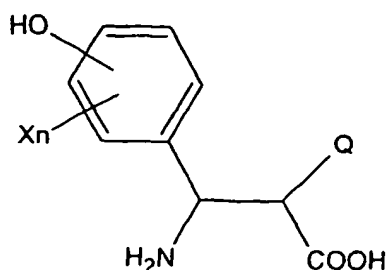


wherein:

- R<sub>4</sub> represents a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> haloalkyl group, linear or branched, optionally substituted; a C<sub>3</sub>-C<sub>6</sub> cycloalkyl group, optionally substituted; an aryl group, optionally substituted; a heteroaryl group, optionally substituted;

(A<sub>6</sub>) :

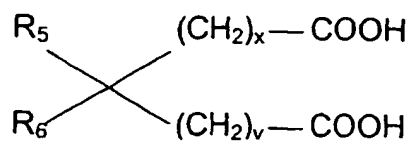
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5 wherein:

- Q, X and n have the same meanings defined above;

(A<sub>7</sub>):



10

wherein:

- R<sub>5</sub> and R<sub>6</sub>, the same or different, represent a hydrogen atom; a halogen atom; a C<sub>1</sub>-C<sub>6</sub> alkyl or C<sub>1</sub>-C<sub>6</sub> haloalkyl group, linear or branched, optionally substituted; a C<sub>2</sub>-C<sub>6</sub> alkenyl or C<sub>2</sub>-C<sub>6</sub> haloalkenyl group, linear or branched, optionally substituted; a C<sub>2</sub>-C<sub>6</sub> alkynyl or C<sub>2</sub>-C<sub>6</sub> haloalkynyl group, linear or branched, optionally substituted; a C<sub>3</sub>-C<sub>6</sub> cycloalkyl group, optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkoxyl or C<sub>1</sub>-C<sub>6</sub> haloalkoxyl group, linear or branched, optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkylthio or C<sub>1</sub>-C<sub>6</sub> haloalkylthio group, linear or branched, optionally substituted; a C<sub>3</sub>-C<sub>6</sub> cycloalkoxyl group, optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkylamine group, linear or branched, optionally substituted; a C<sub>2</sub>-C<sub>12</sub> dialkylamine group, linear or branched, optionally substituted; a C<sub>1</sub>-C<sub>6</sub> alkyl-

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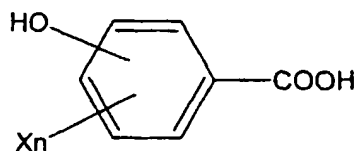
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carbonylamine group, linear or branched, optionally substituted; an arylcarbonylamine group, optionally substituted; an aryl group, optionally substituted; a hetero-aryl group, optionally substituted; a heterocyclic group,  
5 optionally substituted;

- $R_5$  and  $R_6$  can jointly form a  $C_1-C_6$  cycle;
- $x$  and  $y$ , the same or different, are a number ranging from 0 to 4 excluding cases wherein  $x$  and  $y$  are a number ranging from 0 to 2 and  $R_5$  and  $R_6$  are both a hydrogen  
10 atom;

( $A_8$ ):



15 wherein

- $X$  and  $n$  have the same meanings described above excluding salicylic acid; alone or in a mixture, for the control of bacterial and fungal phytopathogens on vegetable or parts thereof.

20 A  $C_1-C_6$  alkyl group refers to a linear or branched  $C_1-C_6$  alkyl group, optionally substituted by one or more substituents, the same or different.

Examples of this group are: methyl, ethyl, propyl, isopropyl, butyl, isobutyl, tert-butyl.

25 A  $C_1-C_6$  haloalkyl group refers to a linear or



branched C<sub>1</sub>-C<sub>6</sub> alkyl group, optionally substituted by one or more halogen atoms, the same or different.

Examples of this group are: fluoromethyl, difluoromethyl, trifluoromethyl, trichloromethyl, 2,2,2-trifluoroethyl, 2,2,2-trichloroethyl, 2,2,3,3-tetrafluoropropyl, 2,2,3,3,3-pentafluoropropyl.

A C<sub>2</sub>-C<sub>6</sub> alkenyl group refers to a linear or branched C<sub>2</sub>-C<sub>6</sub> alkenyl group, optionally substituted by one or more substituents, the same or different.

10 Examples of this group are: ethenyl, propenyl, butenyl.

A C<sub>2</sub>-C<sub>6</sub> haloalkenyl group refers to a linear or branched C<sub>2</sub>-C<sub>6</sub> alkenyl group, optionally substituted by one or more halogen atoms, the same or different.

15 Examples of this group are: 2,2-dichloropropenyl, 1,2,2-trichloropropenyl.

A C<sub>2</sub>-C<sub>6</sub> alkynyl group refers to a linear or branched C<sub>2</sub>-C<sub>6</sub> alkynyl group, optionally substituted by one or more substituents, the same or different.

20 Examples of this group are: ethenyl, propargyl.

A C<sub>2</sub>-C<sub>6</sub> haloalkynyl group refers to a linear or branched C<sub>2</sub>-C<sub>6</sub> alkynyl group, optionally substituted by one or more halogen atoms, the same or different.

Examples of this group are: 3-chloropropinyl.

25 A C<sub>3</sub>-C<sub>6</sub> cycloalkyl group refers to a cycloalkyl

group whose ring consists of 3-6 carbon atoms, optionally substituted by one or more substituents, the same or different.

Examples of this group are: cyclopropyl, 2,2-  
5 dichlorocyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl.

A C<sub>1</sub>-C<sub>6</sub> alkoxy group refers to a C<sub>1</sub>-C<sub>6</sub> alkoxy group, wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> alkyl group, as described above.

Examples of this group are: methoxyl, ethoxyl, iso-  
10 propoxyl, cyclopropyl methoxyl.

A C<sub>1</sub>-C<sub>6</sub> haloalkoxy group refers to a C<sub>1</sub>-C<sub>6</sub> haloalkoxy group, wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> haloalkyl group, as described above.

Examples of this group are: trifluoromethoxyl,  
15 1,1,2,2-tetrafluoroethoxyl, 1,1,2,3,3,3-hexafluoropropoxy.

A C<sub>1</sub>-C<sub>6</sub> thioalkyl group refers to a C<sub>1</sub>-C<sub>6</sub> thioalkyl group, wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> alkyl group, as described above.

20 Examples of this group are: thiomethyl, thioethyl.

A C<sub>1</sub>-C<sub>6</sub> halothioalkyl group refers to a C<sub>1</sub>-C<sub>6</sub> halothioalkyl group, wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> haloalkyl group, as described above.

Examples of this group are: trifluorothiomethoxyl,  
25 1,1,2,2-tetrafluorothioethoxyl.

A C<sub>1</sub>-C<sub>6</sub> alkylsulfinyl group refers to a C<sub>1</sub>-C<sub>6</sub> alkylsulfinyl group, wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> alkyl group, as described above.

Examples of this group are: methylsulfinyl, ethylsulfinyl.

A C<sub>1</sub>-C<sub>6</sub> alkylsulfonyl group refers to a C<sub>1</sub>-C<sub>6</sub> alkylsulfonyl group, wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> alkyl group, as described above.

Examples of this group are: methylsulfonyl, ethylsulfonyl.

A C<sub>3</sub>-C<sub>6</sub> cycloalkoxyl group refers to a C<sub>3</sub>-C<sub>6</sub> cycloalkoxyl group, wherein the aliphatic portion is a C<sub>3</sub>-C<sub>6</sub> cycloalkyl group, as described above.

Examples of this group are: cyclopentoxo, cyclohexyloxy.

A C<sub>1</sub>-C<sub>6</sub> alkylamine or C<sub>2</sub>-C<sub>12</sub> dialkylamine group refers to an alkylamine or dialkylamine group wherein the aliphatic portion is one or two C<sub>1</sub>-C<sub>6</sub> alkyl groups as defined above.

Examples of this group are: methylamino, dimethylamino, ethylamino, isopropylamino, dibutylamino.

An aryl group refers to an aromatic carbocyclic group optionally substituted by one or more groups, the same or different.

Examples of this group are: phenyl, naphthyl.

A heteroaryl group refers to an aromatic penta or

hexatomic heterocyclic group, also benzocondensed or heterobicyclic, containing from 1 to 4 heteroatoms selected from nitrogen, oxygen, sulfur, optionally substituted by one or more groups, the same or different.

5        Examples of heteroaryl groups are: pyridine, pyrimidine, pyridazine, pyrazine, triazine, tetrazine, quinoline, quinoxaline, quinazoline, furan, thiophene, pyrrol, oxazole, thiazole, isoxazole, isothiazole, oxadiazole, thiadiazole, pyrazole, imidazole, triazole, tetra-  
10 zole, indole, benzofuran, benzothiophene, benzoxazole, benzothiazole, benzoxadiazole, benzothiadiazole, benzopyrazole, benzimidazole, benzotriazole, triazolepyridine, triazolepyrimidine, thiazoletriazole.

A heterocyclic group refers to a saturated or unsaturated ring with from three to twelve elements, containing at least one heteroatom selected from nitrogen, oxygen, sulfur, optionally condensed with another aromatic or non aromatic ring.

Examples of heterocyclic rings are: pyrrolidine,  
20 piperidine, dihydropyridine, piperazine, 2,6-diketopiperazine, 2-ketoazetidine, morpholines, thiazine, indoline.

A C<sub>1</sub>-C<sub>6</sub> alkylimine group refers to an alkylimine group wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> alkyl  
25 group as defined above.

Examples of this group are: ethylimine, isopropylimine, benzylimine, 1-phenylethylimine.

An arylimine and heteroarylimine group refers to an arylimine and heteroarylimine group wherein the aromatic  
5 and heteroaromatic portion are an aryl group and a heteroaryl group respectively as defined above.

Examples of this group are: phenylimine, naphthylimine, 2-pyridylimine, 4-pyridylimine, 2-pyrimidylimine, 2-thienylimine, 2-thiazolylimine.

10 A C<sub>1</sub>-C<sub>6</sub> alkoxyimine group refers to an alkoxyimine group wherein the alkoxyl portion is a C<sub>1</sub>-C<sub>6</sub> alkoxyl group as defined above.

Examples of this group are: methoxyimine, ethoxyimine, isopropoxyimine, benzyloxyimine.

15 An aryloxyimine group refers to an aryloxyimine group wherein the aromatic portion is an aryl group as defined above.

Examples of this group are: phenoxyimine, naphthoxyimine.

20 A C<sub>1</sub>-C<sub>6</sub> alkylcarbonylamine group refers to an alkylcarbonylamine group wherein the aliphatic portion is a C<sub>1</sub>-C<sub>6</sub> alkyl group as defined above.

Examples of this group are: acetylamine, propylcarbonylamine.

25 An arylcarbonylamine group refers to an arylcarbon-

ylamine group wherein the aromatic portion is an aryl group as defined above.

Examples of this group are: benzoylamine, 4-methylbenzoylamine.

- 5        A  $C_1$ - $C_6$  alkylcarbonyl group refers to an alkylcarbonyl group wherein the aliphatic portion is a  $C_1$ - $C_6$  alkyl group as defined above.

Examples of this group are: acetyl, ethylcarbonyl, isopropylcarbonyl.

- 10       A  $C_1$ - $C_6$  haloalkylcarbonyl group refers to a haloalkylcarbonyl group wherein the aliphatic portion is a  $C_1$ - $C_6$  haloalkyl group as defined above.

Examples of this group are: 1,1,1-trifluoromethylcarbonyl.

- 15       A  $C_1$ - $C_6$  alkoxy carbonyl group refers to an alkoxy-carbonyl group wherein the aliphatic portion is a  $C_1$ - $C_6$  alkoxyl group as defined above.

Examples of this group are: methoxycarbonyl, ethoxycarbonyl, isopropoxycarbonyl, butoxycarbonyl, benzylloxycarbonyl.

20

- A  $C_1$ - $C_6$  alkylaminocarbonyl or  $C_2$ - $C_{12}$  dialkylaminocarbonyl group refers to an alkylaminocarbonyl or dialkylaminocarbonyl group wherein the aliphatic portion is one or two  $C_1$ - $C_6$  alkyl groups respectively, as defined
- 25 above.

Examples of this group are: methylaminocarbonyl, dimethylaminocarbonyl, ethylaminocarbonyl, isopropylaminocarbonyl, dibutylaminocarbonyl.

Optionally substituted, in all parts of the patent,  
5 refers to one or more substituents, the same or different, selected from the following groups: halogen atoms; C<sub>1</sub>-C<sub>6</sub> alkyls, C<sub>1</sub>-C<sub>6</sub> alkoxy, and C<sub>1</sub>-C<sub>6</sub> alkylthio, C<sub>1</sub>-C<sub>6</sub> alkylsulfinyl and C<sub>1</sub>-C<sub>6</sub> alkylsulfonyl, in turn optionally substituted by halogen atoms; C<sub>1</sub>-C<sub>6</sub> alkyl carbonyls and  
10 C<sub>1</sub>-C<sub>6</sub> alkoxy-carbonyls, optionally halogenated; aminocarbonyls, C<sub>1</sub>-C<sub>6</sub> alkylaminocarbonyls, C<sub>2</sub>-C<sub>12</sub> dialkylaminocarbonyls, optionally halogenated; carboxyl; C<sub>1</sub>-C<sub>6</sub> alkylcarbonyloxy optionally halogenated; cyano; nitro; formyl; hydroxyl; amino; aryl and heteroaryl, optionally substituted.  
15

Examples of compounds having general formula (I) which are interesting for their activity are:

- copper (II) salt of 4-chlorobenzylidenemalononic acid;
- copper (II) salt of 4-hydroxy-3-methoxybenzylidene  
20 malonic acid;
- copper (II) salt of 3,4-dimethoxybenzylidenemalononic acid;
- copper (II) salt of 4-fluorobenzylidenemalononic acid;
- copper (II) salt of 4-trifluoromethylbenzylidenemalononic acid;  
25

- copper (II) salt of 4-dimethylaminobenzylidenemalonic acid;
- copper (II) salt of 2,4-dichlorobenzylidenemalonic acid;
- 5 • copper (II) salt of 4-bromobenzylidenemalonic acid;
- copper (II) salt of 4-hydroxy-3-methoxybenzylidene malonic acid monomethyl ester;
- copper (II) salt of 4-hydroxy-3-methoxybenzylidenemalonic acid monoethyl ester;
- 10 • copper (II) salt of 2-cyano-3-(4-hydroxy-3-methoxyphenyl)propenoic acid;
- copper (II) salt of 2-acetyl-3-(4-hydroxy-3-methoxyphenyl)propenoic acid;
- copper (II) salt of 2-aminocarbonyl-3-(4-hydroxy-3-methoxyphenyl)propenoic acid;
- 15 • copper (II) salt of 3-(4-hydroxy-3-methoxyphenyl)-2-methoxycarbonyl-2-butenic acid;
- copper (II) salt of 4-hydroxy-3-methoxy cinnamic acid;
- 20 • copper (II) salt of 2-hydroxycinnamic acid;
- copper (II) salt of 3-hydroxycinnamic acid;
- copper (II) salt of 4-hydroxycinnamic acid;
- copper (II) salt of 3-ketoglutaric acid;
- copper (II) salt of 3-methoxy-2-pentendioic acid;
- 25 • copper (II) salt of 3-amino-2-carboxy-3-(4-chloro-



- phenyl)propanoic acid;
- copper (II) salt of 3-amino-2-carboxy-3-(2-hydroxy-phenyl)propanoic acid;
  - copper (II) salt of 3-amino-2-carboxy-3-(4-trifluoro  
5 methylphenyl)propanoic acid;
  - copper (II) salt of 3-amino-2-carboxy-3-(4-hydroxy-3-methoxyphenyl)propanoic acid;
  - copper (II) salt of 3-amino-2-carboxy-3-(3,4-dimethoxyphenyl)propanoic acid;
  - 10 • copper (II) salt of 3-amino-3-(2-hydroxyphenyl)propanoic acid;
  - copper (II) salt of 3-amino-3-(4-hydroxy-3-methoxyphenyl)propanoic acid;
  - copper (II) salt of 3-amino-2-cyano-3-(4-  
15 hydroxyphenyl)propanoic acid;
  - copper (II) salt of 3-amino-2-cyano-3-(4-hydroxy-3-methoxyphenyl)propanoic acid;
  - copper (II) salt of 2-methoxysuccinic acid;
  - copper (II) salt of 2-ethoxysuccinic acid;
  - 20 • copper (II) salt of 3-(2-furyl)-2-carboxypropenoic acid;
  - copper (II) salt of 3-(2-thiazolyl)-2-carboxypropenoic acid;
  - copper (II) salt of 3-benzylidene-2-carboxypropenoic  
25 acid;

- copper (II) salt of 1,1-cyclopropane dicarboxylic acid;
- copper (II) salt of diallylmalonic acid;
- copper (II) salt of ethylphenyl malonic acid;
- 5 • copper (II) salt of bis(2-cyano ethyl)malonic acid;
- copper (II) salt of N-morpholine malonic acid;
- copper (II) salt of N-benzyloxyimino malonic acid;
- copper (II) salt of 3-hydroxy benzoic acid;
- copper (II) salt of 4-hydroxy benzoic acid;
- 10 • copper (II) salt of 5-chloro-2-hydroxy benzoic acid;
- copper (II) salt of 5-bromo-2-hydroxy benzoic acid;
- copper (II) salt of 2-hydroxy-3-methoxy benzoic acid;
- copper (II) salt of 2-hydroxy-5-methoxy benzoic acid;
- 15 • copper (II) salt of 2-hydroxy-3-methyl benzoic acid;
- copper (II) salt of 4-hydroxy-3-methoxy benzoic acid;
- copper (II) salt of 3,5-dimethoxy-4-hydroxy benzoic acid;
- 20 • copper (II) salt of 3,5-dichloro-4-hydroxy benzoic acid;
- copper (II) salt of 3,5-dibromo-4-hydroxy benzoic acid;
- 25 • copper (II) salt of 3,5-dimethyl-4-hydroxy benzoic acid;

acid;

- copper (II) salt of 3-chloro-4-hydroxy benzoic acid;
- copper (II) salt of 2,3-dihydroxy benzoic acid;
- copper (II) salt of 2,6-dihydroxy benzoic acid;
- 5 • copper (II) salt of 3,4-dihydroxy benzoic acid.

An object of the present invention also relates to the use of the compounds having general formula (I) for the control of fungal phytopathogens on non-living substrates such as plastics, metals, textile fibres, glass,  
10 wood, paper, foams, bricks.

As specified above, many of the salts of formula (I) are new products.

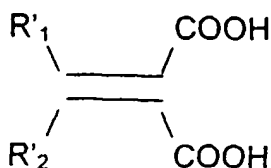
A further object of the present invention therefore relates to the compounds having general formula (I'):



wherein:

- A' represents the bibasic ion of an organic acid which can have the meanings (A'<sub>1</sub>)-(A'<sub>7</sub>);
- 20 - Cu represents the copper 2+ ion;
- (A'<sub>1</sub>)-(A'<sub>7</sub>) respectively represent the following carboxylic acids:

- (A'<sub>1</sub>):



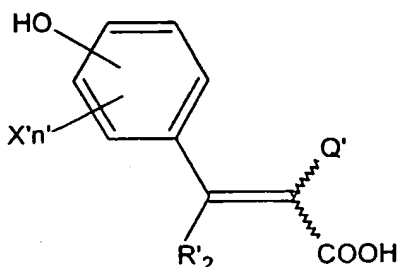
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wherein:

- $R'_1$  represents an aryl group optionally substituted;
- $R'_2$  represents a hydrogen atom;

• ( $A'_2$ ):

5



10 wherein:

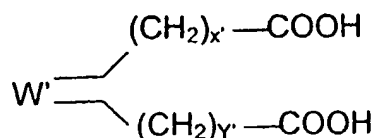
- $X'$  represents a hydrogen or halogen atom; a hydroxyl group; a  $C_1$ - $C_6$  alkoxy group, linear or branched, optionally substituted;
- $n'$  can have the value of 1 or 2;

15 -  $R'_2$  represents a hydrogen atom;

- $Q'$  represents a hydrogen atom; a  $C_1$ - $C_6$  alkoxycarbonyl group, linear or branched, optionally substituted; an acetyl group; a cyano group;

• ( $A'_3$ ):

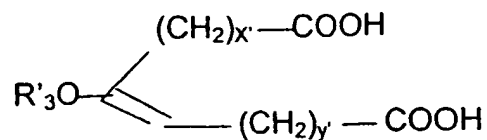
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wherein:

- $W'$  represents an oxygen atom;
- 25 -  $x'$  and  $y'$  both have the value of 1;

- (A'<sub>4</sub>) :

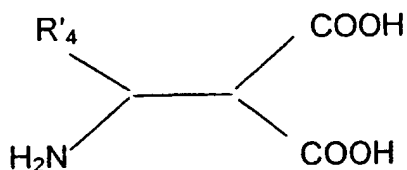


5 wherein:

- R'<sub>3</sub> represents a C<sub>1</sub>-C<sub>3</sub> alkyl group, linear or branched;
- x' is equal to 1 and y' is equal to 0;

- (A'<sub>5</sub>) :

10

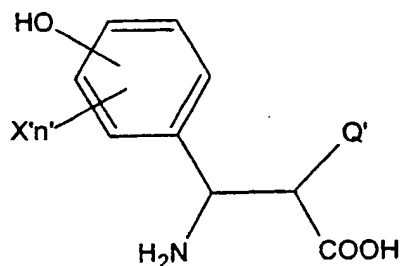


wherein:

- 15 - R'<sub>4</sub> represents an aryl group, optionally substituted;

- (A'<sub>6</sub>) :

20

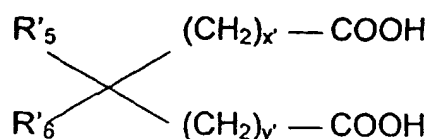


wherein:

- X' represents a hydrogen or halogen atom; a hydroxyl group; a C<sub>1</sub>-C<sub>6</sub> alkoxyl group, linear or branched, option-
- 25 ally substituted;

- n' can have the value of 1 or 2;
- Q' represents a hydrogen atom; a C<sub>1</sub>-C<sub>6</sub> alkoxy carbonyl group, linear or branched, optionally substituted; an acetyl group; a cyano group;

5 • (A' <sub>7</sub>) :



wherein:

- 10 - R'<sub>5</sub> represents a C<sub>1</sub>-C<sub>6</sub> alkoxyl group, linear or branched;
- R'<sub>6</sub> represents a hydrogen atom;
  - x' is equal to 0 and y' is equal to 1.

Examples of products having general formula (I')

15 which have never been described before are:

- copper (II) salt of 4-chlorobenzylidenemalonic acid;
- copper (II) salt of 4-hydroxy-3-methoxybenzylidene malonic acid;
- copper (II) salt of 3,4-dimethoxybenzylidene malonic acid;
- 20 • copper (II) salt of 4-fluorobenzylidene malonic acid;
- copper (II) salt of 4-trifluoromethylbenzylidene malonic acid;
- 25 • copper (II) salt of 4-dimethylaminobenzylidene malo-

nic acid;

- copper (II) salt of 2,4-dichlorobenzylidene malonic acid;
- copper (II) salt of 4-bromobenzylidene malonic acid;
- 5 • copper (II) salt of 4-hydroxy-3-methoxybenzylidene malonic acid monomethyl ester;
- copper (II) salt of 4-hydroxy-3-methoxybenzylidene malonic acid monoethyl ester;
- copper (II) salt of 2-cyano-3-(4-hydroxy-3-methoxyphenyl)propenoic acid;
- 10 • copper (II) salt of 2-acetyl-3-(4-hydroxy-3-methoxyphenyl)propenoic acid;
- copper (II) salt of 2-aminocarbonyl-3-(4-hydroxy-3-methoxyphenyl)propenoic acid;
- 15 • copper (II) salt of 3-(4-hydroxy-3-methoxyphenyl)-2-methoxycarbonyl-2-butenic acid;
- copper (II) salt of 4-hydroxy-3-methoxy cinnamic acid;
- copper (II) salt of 2-hydroxycinnamic acid;
- 20 • copper (II) salt of 3-hydroxycinnamic acid;
- copper (II) salt of 4-hydroxycinnamic acid;
- copper (II) salt of 3-ketoglutaric acid;
- copper (II) salt of 3-methoxy-2-pentendioic acid;
- copper (II) salt of 3-amino-2-carboxy-3-(4-chloro-phenyl)propanoic acid;
- 25

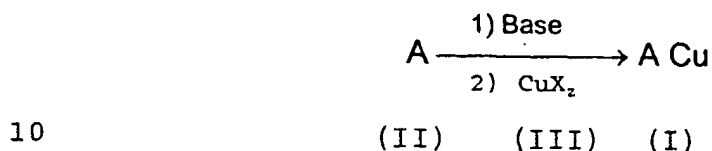
- copper (II) salt of 3-amino-2-carboxy-3-(2-hydroxyphenyl)propanoic acid;
- copper (II) salt of 3-amino-2-carboxy-3-(4-trifluoromethylphenyl)propanoic acid;
- 5 • copper (II) salt of 3-amino-2-carboxy-3-(4-hydroxy-3-methoxyphenyl)propanoic acid;
- copper (II) salt of 3-amino-2-carboxy-3-(3,4-dimethoxyphenyl)propanoic acid;
- copper (II) salt of 3-amino-3-(2-hydroxyphenyl)propanoic acid;
- 10 • copper (II) salt of 3-amino-3-(4-hydroxy-3-methoxyphenyl)propanoic acid;
- copper (II) salt of 3-amino-2-cyano-3-(4-hydroxyphenyl)propanoic acid;
- 15 • copper (II) salt of 3-amino-2-cyano-3-(4-hydroxy-3-methoxy phenyl)propanoic acid;
- copper (II) salt of 2-methoxysuccinic acid;
- copper (II) salt of 2-ethoxysuccinic acid;
- copper (II) salt of 3-(2-furyl)-2-carboxypropenoic acid;
- 20 • copper (II) salt of 3-(2-thiazolyl)-2-carboxypropenoic acid;
- copper (II) salt of 3-benzylidene-2-carboxypropenoic acid;
- 25 • copper (II) salt of diallylmalonic acid;



- copper (II) salt of ethylphenylmalonic acid;
- copper (II) salt of bis(2-cyano ethyl)malonic acid;
- copper (II) salt of N-morpholine malonic acid;
- copper (II) salt of N-benzyloxyiminomalonic acid;

5       The compounds having formula (I) can be easily obtained according to the reaction scheme A:

Scheme A



wherein A has the same meanings defined above and z has the value of 1 or 2.

The compounds having general formula (I) can be obtained by dissolving the organic carboxylic acid having  
 15 general formula (II) in water using at least two equivalents of an inorganic base such as sodium or potassium bicarbonate, sodium or potassium or calcium hydroxide, and adding an aqueous solution of a copper salt having  
 formula (III) to the resulting mixture, wherein X can be  
 20 a halogen, such as chlorine or bromine, or a perchlorate, (Z = 2); or a sulfate ion, (z = 1) to give a compound having formula (I).

Alternatively, it is possible to use copper hydroxide or carbonate (in these cases X represents an OH group  
 25 or a CO<sub>3</sub> group respectively and z has the value of 2 or 1

respectively) in the presence of the acid form (II), optionally in the presence of an additional base, such as for example, an organic amine such as triethylamine.

Alternatively, the compounds having general formula  
5 (I) can be obtained by the saponification of esters corresponding to the organic carboxylic acids having general formula (II), in water and alcohol according to the traditional synthesis procedures, and subsequent addition to the resulting mixture of an aqueous solution of a copper  
10 salt having formula (III) as described above.

The carboxylic acids having general formula (II), when not known in themselves, can be prepared according to methods known in literature, according to what is described, for example, in: Organic Reactions (1967), vol.  
15 15, page 204; or in Proc. Indian Acad. Sci. (1941), vol. 14A, pages 112-122; or in J. Org. Chem. (1979), vol. 44, page 3136.

If the organic acids corresponding to general formula (II) contain optical or geometric isomerism centres,  
20 the compounds having general formula (I) can be present in all possible configurational isomeric forms.

The scope of the present invention therefore also includes the use of compounds having general formula (I) as isomeric mixtures in any proportion, as well as the  
25 production and use of the single isomers for the control

of phytopathogen fungi in the agronomical field.

The compounds having general formula (I) can also be present in hydrated form by the coordination of a any number of molecules of water.

5       The compounds having general formula (I) can also coordinate within their structure metallic cations, such as, for example, sodium, calcium, potassium, whose number can vary in relation to the preparation method used for the synthesis of the cupric salt having general formula  
10 (I) and they can possibly be present in the hydrated form.

The use of these mixed salts for the control of phytopathogen fungi in the agronomical field, also falls within the scope of the present invention.

15       The copper salts of carboxylic acids having general formula (I) are capable of controlling many fungal and bacterial phytopathogens, also with a reduced sensitivity towards other fungicides.

Some examples of phytopathogens controlled by the  
20 compounds having general formula (I) alone or in a mixture, are listed below for purely illustrative and non-limiting purposes, together with examples of possible application crops:

- *Plasmopara viticola* on vines;
- 25 - *Phytophthora* spp. on vegetables;

- *Pyricularia oryzae* on rice;
- *Venturia inaequalis* on apples;
- *Peronospora tabacina* on tobacco;
- *Pseudoperonospora cubensis*. on cucurbitaceous products;
- *Bremia* on salads, spinach;
- *Alternaria spp.* on tomatoes, potatoes.

The cupric salts having general formula (I) are capable of exerting a high fungicidal action of both a curative and preventive nature and they also have a low phyto-toxicity or absence thereof.

A further object of the present invention therefore relates to a method for the control of phytopathogen fungi in agricultural crops by the application of compounds having general formula (I).

The quantity of compound to be applied for obtaining the desired effect can vary in relation to several factors, such as, for example, the compound used, the crop to be preserved, the type of pathogen, the degree of infection, the climatic conditions, the application method, the formulation adopted.

Dosages of compound ranging from 10 g to 5 kg per hectare, generally provide a sufficient control.

For practical use in agriculture, it is often convenient to adopt fungicidal compositions containing one

or more of the compounds having general formula (I).

The application of these compositions or compounds having general formula (I) can be effected on any part of the plant, for example on the leaves, stems, branches and  
5 roots, or on the seeds before being planted, or on the ground in which the plant grows.

Compositions can be used which are in the form of dry powders, wettable powders, emulsifiable concentrates, micro-emulsions, pastes, granulates, solutions, suspen-  
10 sions, etc.: the selection of the type of composition will depend on the specific use.

The compositions are prepared according to known methods, for example by diluting or dissolving the active substance with a solvent and/or solid diluent, possibly  
15 in the presence of surfactants.

Silica, kaolin, bentonite, talc, infusorial earth, dolomite, calcium carbonate, magnesia, chalk, clays, synthetic silicates, attapulgite, sepiolite, can be used as solid diluents, or carriers.

20 In addition to water, aromatic organic solvents (xylools or mixtures of alkyl benzols, chlorobenzene, etc.), paraffins (oil fractions), alcohols (methanol, propanol, butanol, octanol, glycerin, etc.), esters (ethyl acetate, isobutyl acetate, etc.), ketones (cyclohexanone, acetone,  
25 acetophenone, isophorone, ethyl amyl ketone, etc.), am-

ides (N,N-dimethyl formamide, N-methyl pyrrolidone, etc.), can be used as liquid diluents.

Sodium, calcium, triethyl amine or triethanol amine salts of alkyl sulphonates, alkyl aryl sulphonates, poly-  
5 ethoxylated alkyl phenols, polyoxyethylated esters of sorbitol, lignin sulfonates, etc., can be used as surfactants.

The compositions can also contain special additives for particular purposes, such as, for example, adhesion  
10 agents, such as gum Arabic, polyvinyl alcohol, polyvinyl pyrrolidone, polyacrylates.

In the above compositions, the concentration of active substances ranges from 0.1 to 98%, preferably from 0.5 to 90%.

15 Other compatible active principles can be added, if desired, to the compounds having general formula (I), such as, for example, fungicides, phyto-regulators, antibiotics, herbicides, insecticides, fertilizers.

Examples of other fungicides which can be included  
20 in the compositions of the invention are:

AC-382042, acibenzolar, ampropylfos, anilazine, azaconazole, azoxystrobin, benalaxyl (in its racemic form or as optically active R isomer), benclothiaz, benomyl, bitertanol, blasticidin-S, bromuconazole, bupirimate,  
25 buthiobate, captafol, captan, carbendazim, carboxin, car-

propamid, chinomethionat, chloroneb, chlorothalonil, chlozolate, cuprocalcic, cyazofamid, cymoxanil, cyproconazole, cyprodinil, debacarb, dichlofluanid, dichlone, diclobutrazol, diclomezine, dicloran, diclocymet, diethofencarb, diphenconazole, diflumetorim, dimethirimol, dimethomorph, diniconazole, dinocap, a fungicidal dipeptide, dipyrithione, ditalimfos, dithianon, dodemorph, dodine, edifenphos, epoxiconazole, etaconazole, ethaboxam, ethirimol, ethoxyquin, etridiazole, famoxadone, fenamidone, fenaminosulf, fenapanil, fenarimol, fenbuconazole, fenfuram, fenhexamid, fenoxanil, fenciclonil, fenpropidin, fenpropimorph, fentin, ferbam, ferimzone, fluazinam, fludioxonil, flumetover, flumorph, fluoroimide, fluotrimazole, fluoxastrobin, fluquinconazole, flusilazole, flusulfamide, flutolanil, flutriafol, folpet, fosetylaluminium, fuberidazole, furalaxyl, furconazole, guazatine, hexaconazole, hydroxyquinoline sulfate, hymexazol, ICIA0858, imazalil, imibenconazole, iminocadine, ipconazole, iprobenfos, iprodione, isoprothiolane, iprovalicarb, kasugamycin, kresoxim-methyl, mancopper, mancozeb, maneb, mebenil, mepanipyrim, mepronil, metalaxyl, metalaxyl-M, metconazole, methfuroxam, metiram, metsulfovax, MON-65500, myclobutanil, natamycin, nicobifen, nitrothal-isopropyl, nuarimol, ofurace, orisastrobin, tetraramic oxychloride, oxadixyl, oxycar-

boxin, pefurazoate, penconazole, pencycuron, pentachloro-  
phenol and its salts, penthiovalicarb, phthalide, piper-  
alin, Bordeaux mixture, polyoxins, probenazole, pro-  
chloraz, procymidone, propamocarb, propiconazole, pro-  
5 pineb, proquinazid, prothiocarb, prothioconazole, pycox-  
ystrobin, pyracar-bolid, pyraclostrobin, pyrazophos,  
pyrifenox, pyrimethanil, pyroquilon, pyroxyfur, quinace-  
tol, quinazamid, quinconazole, quinoxifen, quintozene,  
rabenazole, copper hydroxide, copper oxychloride, copper  
10 sulfate, RH-7281, RPA-407213, simeconazole, spiroxamine,  
spiromesifen, SSF-126, (metominostrobin), streptomycin,  
SYP-L-190, tebuconazole, tetraconazole, thiabendazole,  
thicyofen, thifluzamide, thiophanate-methyl, thiram, ti-  
oxymid, tolclofos-methyl, tolylfluanid, triadimefon, tri-  
15 adimenol, triarimol, triazbutil, triazoxide, tricycla-  
zole, tridemorf, trifloxystrobin (CGA 279202),  
triflumizole, triforine, triticonazole, validamycin, vin-  
clozolin, zineb, ziram, sulfur, zoxamide.

These fungicidal compounds are commercial products  
20 or products about to be commercialized. Their description  
can be easily found in technical literature, for example  
in "The pesticide manual", 2000, XII Edition, British  
Crop Protection Council Ed.

Dipeptide with a fungicidal activity refers to  
25 one of the compounds among those claimed in patent appli-



cation EP-A-1028125.

It has also been found that the salts of derivatives of carboxylic acids having general formula (I), also exert a synergic action with many of the active principles listed above, thus representing an excellent instrument for anti-resistance strategies and allowing a further lowering in the applicative dosages.

The following examples are provided for illustrative purposes, for a better understanding of the invention, and should in no way be considered as limiting the scope of the present invention.

#### EXAMPLE 1

**Preparation of the copper salt of 4-chlorobenzylidene malonic acid (Compound Nr. 1)**

8 g of 4-chlorobenzylidenemalonic acid are added to a solution of 5.95 g of sodium bicarbonate in 140 cm<sup>3</sup> of water. After the complete dissolution of the acid, a solution of 8.74 g of copper sulfate in 20 cm<sup>3</sup> of water, are added to the reaction mixture. The mixture is kept under stirring at room temperature for a night. The solid precipitated is filtered and washed with water, obtaining, after drying in the air, 8.85 g of compound Nr. 1 (yield: 88%).

Elemental analysis [% found (theoretical)]=

C 41.1 (41.7); H 1.9 (1.7); Cl 12.3 (12.7); Cu 21.9

(22.1).

## EXAMPLE 2

Preparation of the copper salt of 4-hydroxy-3-methoxybenzylidene malonic acid monomethyl ester (Compound Nr. 50).

17.8 cm<sup>3</sup> of a 3.1 N solution of NaOH are slowly added dropwise on an ice bath to a suspension of 7.4 g of 4-hydroxy-3-methoxybenzylidene malonic acid dimethyl ester in 8 cm<sup>3</sup> of methanol. The resulting solution is left under stirring for 24 hours at room temperature; a solution of copper sulfate (6.95 g in 16 cm<sup>3</sup> of H<sub>2</sub>O) is then added and the mixture is kept under stirring for a further 24 hours. The solid precipitated is filtered and washed with water, obtaining, after drying in the air, 7.0 g of compound Nr. 47 (yield: 81%).

Elemental analysis [% found (theoretical)]=

C 45.2 (45.9); H 3.1 (3.2); Cu 20.4 (20.2).

## Example 3

Preparation of the copper salt of 3-ketoglutaric acid (Compound Nr. 132).

11.5 g of sodium bicarbonate are added in portions, on an ice bath, to a suspension of 10 g of 3-ketoglutaric acid in 45 cm<sup>3</sup> of H<sub>2</sub>O. 9.1 g of copper (II) chloride are then added, again on an ice bath. The reaction mixture is left under stirring for 24 hours at room temperature. The

solid precipitated is filtered and washed with water, obtaining, after drying in the air, 12.0 g of compound Nr. 129 (yield 83%).

Elemental analysis [% found (theoretical)]=

5 C 28.2 (28.9); H 2.0 (1.9); Cu 30.7 (30.6).

#### Example 4

Preparation of the copper salt of 2-methoxysuccinic acid (Compound Nr. 239).

10 g of dimethyl maleate are added under stirring to  
10 25 cm<sup>3</sup> of a 3 M methanol solution of MeONa. After an hour, 10 cm<sup>3</sup> of a 7 N solution of NaOH are added dropwise and after another hour a solution of copper sulfate (17.2 g in 45 cm<sup>3</sup> of H<sub>2</sub>O) is added. The reaction mixture is kept under stirring for a further 24 hours. The solid  
15 precipitated is filtered and washed with water, obtaining, after drying in the air, 11.2 g of compound Nr. 235 (yield 80%).

Elemental analysis [% found (theoretical)]=

C 28.3 (28.6); H 2.7 (2.9); Cu 29.9 (30.3).

#### 20 Example 5

Preparation of the copper salt of 5-chlorosalicylic acid (Compound Nr. 275).

10 cm<sup>3</sup> of a 5.8 N solution of NaOH are added to a suspension of 5 g of 5-chlorosalicylic acid in 10 cm<sup>3</sup> of  
25 H<sub>2</sub>O. After the complete dissolution of the acid, a solu-

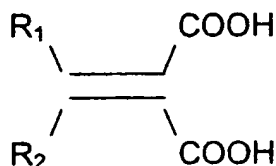
tion of copper chloride (3.9 g in 40 cm<sup>3</sup> of H<sub>2</sub>O) is added. The reaction mixture is kept under stirring for 24 hours. The solid precipitated is filtered and washed with water, obtaining, after drying in the air, 6.3 g of compound Nr. 269 (yield 93%).

Elemental analysis [% found (theoretical)]=  
C 35.4 (35.9); H 1.25 (1.3); Cl 15.1 (14.9); Cu 26.9 (27.1).

Analogously to what is described in the examples, the following compounds were prepared:

Table 1

Derivatives of general formula (I) wherein A has the meaning of (A<sub>1</sub>):



Compound Nr.	R <sub>1</sub>	R <sub>2</sub>
2	4-OH-3-OCH <sub>3</sub> -phenyl	H
3	3,4-di-OCH <sub>3</sub> -phenyl	H
4	4-F-phenyl	H
5	4-CF <sub>3</sub> -phenyl	H
6	4-CH <sub>3</sub> -phenyl	H
7	4-OCH <sub>3</sub> -phenyl	H

5	8	2,4-diCl-phenyl	H
	9	4-Br-phenyl	H
	10	2-OH-phenyl	H
	11	2,6-diCl-phenyl	H
	12	4-OH-phenyl	H
10	13	4-CH <sub>3</sub> -phenyl	H
	14	2-CF <sub>3</sub> -phenyl	H
	15	4-OH-3-OCH <sub>3</sub> -phenyl	CH <sub>3</sub>
	16	3,4-diOCH <sub>3</sub> -phenyl	CH <sub>3</sub>
	17	4-Cl-phenyl	CF <sub>3</sub>
15	18	4-CF <sub>3</sub> -phenyl	CH <sub>2</sub> CH <sub>3</sub>
	19	4-OH-3-OCH <sub>3</sub> -phenyl	phenyl
	20	3,4-diOCH <sub>3</sub> -phenyl	phenyl
	21	4-Cl-phenyl	phenyl
	22	4-OH-3-OCH <sub>3</sub> -phenyl	cyclopentyl
20	23	3,4-diOCH <sub>3</sub> -phenyl	cyclopropyl
	24	4-OCF <sub>3</sub> -phenyl	H
	25	1-naphthyl	H
	26	4-N(CH <sub>3</sub> ) <sub>2</sub> phenyl	H
	27	Cyclopentyl	H
25	28	Cyclohexyl	H
	29	3,4-methylenedioxyphenyl	H
	30	CH <sub>3</sub>	CH <sub>3</sub>
	31	Isopropyl	H
	32	Benzyl	H
	33	CF <sub>3</sub>	H
	34	Isobutyl	CH <sub>3</sub>
	35	2-(phenyl)ethyl	H
	36	1-(phenyl)ethyl	H

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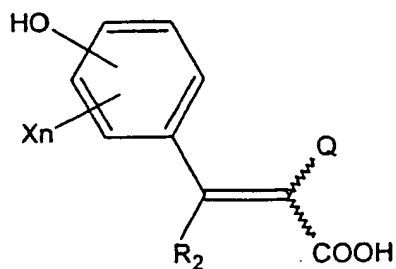
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37	2-furyl	H
38	2-thiazolyl	H
39	2-furyl	CH <sub>3</sub>
40	2-thiazolyl	CH <sub>3</sub>
41	2-pyridyl	H
42	2-pyridyl	CH <sub>3</sub>
43	4-pyridyl	CH <sub>3</sub>
44	4-pyridyl	H
45	2-pyrimidyl	H
46	benzylidene	H
47	2-Cl-phenyl	H
48	ethoxyl	H
49	phenyl	H

Table 2

Derivatives of general formula (I) wherein A has the  
 15 meaning of (A<sub>2</sub>):

20



25

Comp. Nr.	OH pos.	X	n	R <sub>2</sub>	Q
51	4	3-OCH <sub>3</sub>	1	H	CN
52	4	3-OCH <sub>3</sub>	1	H	H
53	4	3-OCH <sub>3</sub>	1	H	COCH <sub>3</sub>

Comp. Nr.	OH pos.	X	n	R <sub>2</sub>	Q
54	4	3-OCH <sub>3</sub>	1	H	CONH <sub>2</sub>
55	4	3-OCH <sub>3</sub>	1	CH <sub>3</sub>	COOCH <sub>3</sub>
56	4	3-OCH <sub>3</sub>	1	H	COOCH <sub>2</sub> CH <sub>3</sub>
57	4	3-OCH <sub>3</sub>	1	H	COOCH(CH <sub>3</sub> ) <sub>2</sub>
58	4	3-OCH <sub>3</sub>	1	H	CONHCH <sub>3</sub>
59	4	3-OCH <sub>3</sub>	1	H	CON(CH <sub>3</sub> ) <sub>2</sub>
60	4	3-OCH <sub>3</sub>	1	H	CH <sub>2</sub> CH <sub>3</sub>
61	4	3-OCH <sub>3</sub>	1	H	CH <sub>3</sub>
62	4	3-OCH <sub>3</sub>	1	H	CF <sub>3</sub>
63	4	3-OCH <sub>3</sub>	1	H	COOCH <sub>2</sub> Ph
64	4	3-OCH <sub>3</sub>	1	H	COCF <sub>3</sub>
65	4	3-OCH <sub>3</sub>	1	Ph	COCF <sub>3</sub>
66	4	3,5-diOCH <sub>3</sub>	2	H	COOCH <sub>3</sub>
67	4	3,5-diOCH <sub>3</sub>	2	H	H
68	4	3,5-diOCH <sub>3</sub>	2	H	COCH <sub>3</sub>
69	4	3,5-diOCH <sub>3</sub>	2	H	CONH <sub>2</sub>
70	4	3,5-diOCH <sub>3</sub>	2	H	CN
71	4	3,5-diCl	2	H	COOCH <sub>3</sub>
72	4	3,5-diCl	2	H	H
73	4	3,5-diCl	2	H	COCH <sub>3</sub>
74	4	3,5-diCl	2	H	CONH <sub>2</sub>
75	4	3,5-diCl	2	H	CN
76	4	3,5-diBr	2	H	COOCH <sub>3</sub>
77	4	3,5-diBr	2	H	H
78	4	3,5-diBr	2	H	COCH <sub>3</sub>
79	4	3,5-diBr	2	H	CONH <sub>2</sub>
80	4	3,5-diBr	2	H	CN
81	2	5-Cl	1	H	COOCH <sub>3</sub>

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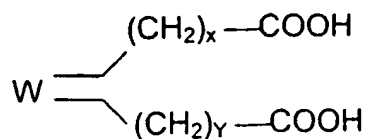
Comp. Nr.	OH pos.	X	n	R <sub>2</sub>	Q
82	2	5-Cl	1	H	CN
83	2	5-Cl	1	H	H
84	2	5-Cl	1	H	COCH <sub>3</sub>
85	2	5-Cl	1	H	CONH <sub>2</sub>
86	2	5-Cl	1	H	COOCH <sub>2</sub> CH <sub>3</sub>
87	2	5-Cl	1	H	CONHCH <sub>3</sub>
88	2	5-Cl	1	H	CON(CH <sub>3</sub> ) <sub>2</sub>
89	2	5-Cl	1	H	CH <sub>2</sub> CH <sub>3</sub>
90	2	5-Cl	1	H	CH <sub>3</sub>
91	2	3-CH <sub>3</sub>	1	H	COOCH <sub>3</sub>
92	2	3-CH <sub>3</sub>	1	CH <sub>3</sub>	COOCH <sub>3</sub>
93	2	3-CH <sub>3</sub>	1	Ph	COOCH <sub>3</sub>
94	2	3-CH <sub>3</sub>	1	H	COOCH <sub>2</sub> CH <sub>3</sub>
95	2	3-CH <sub>3</sub>	1	H	COCF <sub>3</sub>
96	2	3-CH <sub>3</sub>	1	H	CONHCH <sub>3</sub>
97	2	3-CH <sub>3</sub>	1	CH <sub>3</sub>	COOCH <sub>2</sub> Ph
98	2	3-CH <sub>3</sub>	1	H	COOCH <sub>2</sub> Ph
99	2	5-Br	1	H	COCF <sub>3</sub>
100	2	5-Br	1	H	CON(CH <sub>3</sub> ) <sub>2</sub>
101	2	5-Br	1	H	H
102	2	H	1	H	COOCH <sub>3</sub>
103	2	H	1	H	CN
104	2	H	1	CH <sub>3</sub>	CN
105	2	H	1	H	COCH <sub>3</sub>
106	2	H	1	H	CONH <sub>2</sub>
107	2	H	1	H	H
108	2	H	1	H	COCF <sub>3</sub>
109	2	H	1	H	CONHCH <sub>3</sub>
110	2	H	1	H	COOCH <sub>2</sub> Ph
111	2	H	1	H	COOCH(CH <sub>3</sub> ) <sub>2</sub>
112	3	H	1	H	H



Comp. Nr.	OH pos.	X	n	R <sub>2</sub>	Q
113	3	H	1	H	COOCH <sub>3</sub>
114	3	H	1	H	CN
115	3	H	1	H	COCH <sub>3</sub>
116	3	H	1	H	CONH <sub>2</sub>
117	4	H	1	H	H
118	4	H	1	H	COOCH <sub>3</sub>
119	4	H	1	H	CN
120	4	H	1	H	COCH <sub>3</sub>
121	4	H	1	H	CONH <sub>2</sub>
122	4	H	1	H	COOCH <sub>2</sub> CH <sub>3</sub>
123	4	H	1	4-OHPh	COOCH <sub>2</sub> CH <sub>3</sub>
124	4	H	1	H	CONHCH <sub>3</sub>
125	4	H	1	H	CON(CH <sub>3</sub> ) <sub>2</sub>
126	4	H	1	H	CH <sub>2</sub> CH <sub>3</sub>
127	4	H	1	H	CH <sub>3</sub>
128	4	H	1	H	CF <sub>3</sub>
129	4	H	1	H	COCF <sub>3</sub>
130	4	H	1	CH <sub>3</sub>	COOCH <sub>3</sub>
131	4	H	1	CH <sub>3</sub>	CN

Table 3

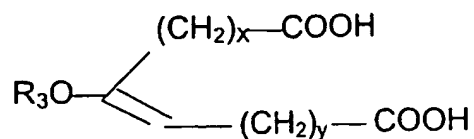
Derivatives of general formula (I) wherein A has the  
 meaning of (A<sub>3</sub>) :



	Comp. Nr.	W	x	y
	133	O	0	0
	134	CH <sub>3</sub> ON	1	1
	135	CH <sub>3</sub> ON	0	0
5	136	CH <sub>3</sub> N	0	0
	137	CH <sub>3</sub> N	0	1
	138	O	1	0
	139	CH <sub>3</sub> N	1	1
	140	EtN	1	1
	141	PhCH <sub>2</sub> N	1	1
10	142	PhN	1	1
	143	4-ClPhN	1	1
	144	PhN	0	0
	145	2-pyridylN	1	1
	146	4-pyridylN	1	1
	147	PhON	1	1
15	148	PhON	0	0
	149	BzON	0	0
	150	CH <sub>3</sub> N	1	2
	151	PhON	1	2
	152	CH <sub>3</sub> ON	1	2
	153	4-ClPhON	1	1
20	154	4-OCH <sub>3</sub> PhON	1	1
	155	4-OCH <sub>3</sub> PhN	1	1
	156	4-CH <sub>3</sub> PhN	1	1

Table 4

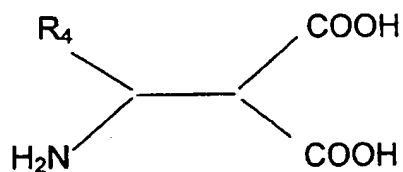
Derivatives of general formula (I) wherein A has the  
 25 meaning of (A<sub>4</sub>) :



Comp. Nr.	R <sub>3</sub>	x	y
157	CH <sub>3</sub>	1	0
158	CH <sub>3</sub>	1	1
159	Ethyl	1	1
160	Benzyl	1	1
161	CH <sub>3</sub>	2	1
162	i-propyl	1	0
163	Benzyl	2	1
164	CH <sub>3</sub>	0	0
165	Ethyl	0	0

Table 5

Derivatives of general formula (I) wherein A has the meaning of (A<sub>5</sub>):

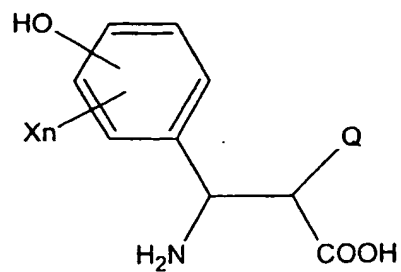


Compound Nr.	R <sub>4</sub>
166	4-Cl-phenyl
167	4-OH-3-OCH <sub>3</sub> -phenyl
168	3,4-diOCH <sub>3</sub> -phenyl
169	4-CF <sub>3</sub> -phenyl
170	4-CH <sub>3</sub> -phenyl

	Compound Nr.	R <sub>4</sub>
	171	4-OCH <sub>3</sub> -phenyl
	172	2,4-diCl -phenyl
	173	4-Br-phenyl
5	174	2-OH-phenyl
	175	2,6-diCl-phenyl
	176	4-OCF <sub>3</sub> -phenyl
	177	2-CF <sub>3</sub> -phenyl
	178	2-pyridyl
	179	4-pyridyl
10	180	2-furyl
	181	2-thiazolyl
	182	2-pyrimidyl
	183	isopropyl
	184	isobutyl
	185	CF <sub>3</sub>
15	186	Cyclopentyl
	187	Cyclopropyl
	188	Cyclohexyl
	189	CH <sub>3</sub>
	190	Benzyl
	191	2-(phenyl)ethyl
20	192	1-(phenyl)ethyl
	193	t-butyl
	194	4-F-phenyl

Table 6

Derivatives of general formula (I) wherein A has the  
 25 meaning of (A<sub>6</sub>):



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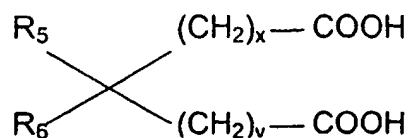
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Comp. Nr.	OH pos.	X	n	Q
195	4	3-OCH <sub>3</sub>	1	CN
196	4	3,5-diOCH <sub>3</sub>	2	CN
197	4	3-OCH <sub>3</sub>	1	H
198	4	3,5-diOCH <sub>3</sub>	2	H
199	4	3-OCH <sub>3</sub>	1	COCH <sub>3</sub>
200	4	3-OCH <sub>3</sub>	1	COCF <sub>3</sub>
201	4	3-OCH <sub>3</sub>	1	CONH <sub>2</sub>
202	4	3-OCH <sub>3</sub>	1	COOCH <sub>2</sub> CH <sub>3</sub>
203	4	3-OCH <sub>3</sub>	1	COOCH(CH <sub>3</sub> ) <sub>2</sub>
204	4	3-OCH <sub>3</sub>	1	CONHCH <sub>3</sub>
205	4	3-OCH <sub>3</sub>	1	CON(CH <sub>3</sub> ) <sub>2</sub>
206	4	3-OCH <sub>3</sub>	1	CH <sub>2</sub> CH <sub>3</sub>
207	4	3-OCH <sub>3</sub>	1	CH <sub>3</sub>
208	4	3-OCH <sub>3</sub>	1	CF <sub>3</sub>
209	4	3-OCH <sub>3</sub>	1	COOCH <sub>2</sub> Ph
210	4	H	1	CN
211	4	H	1	COOCH <sub>2</sub> CH <sub>3</sub>
212	4	H	1	COOCH(CH <sub>3</sub> ) <sub>2</sub>
213	4	H	1	CONHCH <sub>3</sub>
214	4	H	1	CON(CH <sub>3</sub> ) <sub>2</sub>
215	4	H	1	CH <sub>2</sub> CH <sub>3</sub>
216	4	H	1	CH <sub>3</sub>

Comp. Nr.	OH pos.	X	n	Q
217	4	H	1	CF <sub>3</sub>
218	4	H	1	COOCH <sub>2</sub> Ph
219	4	H	1	COCF <sub>3</sub>
220	2	5-Cl	1	CN
221	4	3,5-Cl	2	CN
222	2	5-Cl	1	H
223	4	3,5-Cl	2	H
224	2	5-Cl	1	COCH <sub>3</sub>
225	2	5-Cl	1	CONH <sub>2</sub>
226	2	5-Cl	1	COCF <sub>3</sub>
227	2	5-Cl	1	COOCH <sub>2</sub> CH <sub>3</sub>
228	2	5-Cl	1	COOCH(CH <sub>3</sub> ) <sub>2</sub>
229	2	5-Cl	1	CONHCH <sub>3</sub>
230	2	5-Cl	1	CON(CH <sub>3</sub> ) <sub>2</sub>
231	2	5-Cl	1	CH <sub>2</sub> CH <sub>3</sub>
232	2	5-Cl	1	CH <sub>3</sub>
233	2	5-Cl	1	CF <sub>3</sub>
234	2	3-CH <sub>3</sub>	1	CN
235	2	3-CH <sub>3</sub>	1	CONHCH <sub>3</sub>
236	2	3-CH <sub>3</sub>	1	CON(CH <sub>3</sub> ) <sub>2</sub>
237	2	5-Br	1	H
238	2	H	1	H

Table 7

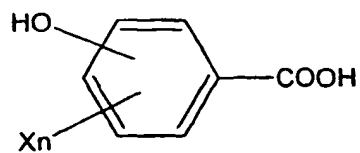
Derivatives of general formula (I) wherein A has the meaning of (A<sub>7</sub>):



Comp. Nr.	R <sub>5</sub>	R <sub>6</sub>	x	y
240	EtO	H	0	1
241	IPrO	H	0	1
242	Allyl	Allyl	0	0
243	2-cyanoethyl	2-cyanoethyl	0	0
244	N-morpholine	H	0	0
245	Ethyl	Phenyl	0	0
246	Methyl	3-OCH <sub>3</sub> -phenyl	0	0
247	Ethyl	Isoamyl	0	0
248	Butyl	Butyl	0	0
249	Cyclopropyl	H	0	0
250	Cyclopentyl	H	0	0
251	4-OH-propyl	4-OH-propyl	0	0
252	CF <sub>3</sub>	Ethyl	0	0
253	CH <sub>3</sub>	2-pyridyl	0	0
254	Hexyl	H	0	0
255	Phenyl	H	0	0
256	Allyl	H	0	0
257	N-propyl	N-propyl	0	0
258	iso-propyl	H	0	0
259	Benzyl	H	0	0
260	Butyl	H	0	0
261	Ethyl	H	0	0
262	3-thienyl	H	0	0
263	N,N-dibutyl	H	0	0
264	t-butyl	H	1	2
265	CH <sub>3</sub>	H	1	2
266	N,N-diethyl	H	0	3
267	PhCONH	H	0	0
268	CH <sub>3</sub> CONH	H	0	0
269	4-CH <sub>3</sub> PhCO	H	0	0
270	2,6-dimethylmorpholine	H	0	0
271	HOCH <sub>2</sub>	HOCH <sub>2</sub>	0	0
272	(CH <sub>3</sub> ) <sub>2</sub> N	H	0	0
273	-CH <sub>2</sub> CH <sub>2</sub> -		0	0
274	-CH <sub>2</sub> CH <sub>2</sub> CH <sub>2</sub> -		0	0

Table 8

Derivatives of general formula (I) wherein A has the  
 meaning of (A<sub>8</sub>):



5	Comp. Nr.	OH pos.	X	n
	276	3	H	1
	277	4	H	1
	278	2	3-OH	1
	279	2	6-OH	1
	280	3	4-OH	1
10	281	2	3-OCH <sub>3</sub>	1
	282	2	5-OCH <sub>3</sub>	1
	283	2	5-Br	1
	284	2	3-CH <sub>3</sub>	1
	285	2	5-F	1
	286	2	5-CN	1
15	287	2	5-CF <sub>3</sub>	1
	288	2	3-NH <sub>2</sub>	1
	289	2	3-N(CH <sub>3</sub> ) <sub>2</sub>	1
	290	4	3,5-diCl	2
	291	4	3,5-diBr	2
	292	4	3,5-diOCH <sub>3</sub>	2
	293	4	3,5-diCH <sub>3</sub>	2
20	294	4	3-OCH <sub>3</sub>	1
	295	4	3-Cl	1
	296	4	3-NO <sub>2</sub>	1

#### Example 6

Determination of the fungicidal activity against peronospora in vines (*Plasmopara viticola*).



Vine plant leaves (cultivar Dolcetto) grown in vases in a conditioned environment ( $20\pm 1^{\circ}\text{C}$ , 70% relative humidity) are treated by spraying both sides of the leaf with compounds 1, 2 and 3, dispersed in a hydro-acetone solution at 20% by volume in acetone.

After remaining 24 hours in a conditioned atmosphere, the plants are sprayed on both sides of the leaf with an aqueous suspension of conidia of *Plasmopara viticola* (20000 conidia per  $\text{cm}^3$ ).

The plants are kept in a humidity saturated environment at  $21^{\circ}\text{C}$  for the incubation period of the fungus.

At the end of said period (7 days), the fungicidal activity is evaluated according to a percentage evaluation scale from 0 (completely infected plant) to 100 (healthy plant).

All the compounds tested showed a fungus control higher than 90 at a concentration of 1000 ppm.